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Progress in carbanionic polymerization via a two-electron transfer mechanism

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The paper is dedicated to Professor Roderic P. Quirk with congratulations on his excellent achievements in polymer chemistry

Abstract

A novel type of catalysts useful in the anionic polymerization processes is demonstrated. Alkali metal ion pairs, e.g. K^+crown ether, K^- discovered first by Dye and Edwards were modified and used as catalysts in the polymerization of isoprene. The reaction mechanism including two-electron transfer to monomer and formation of a carbanion is discussed. The novel type of anionic polymerization yields polyisoprene with well-defined properties. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Anion-promoted reactions are very common in organic chemistry, e.g. in aliphatic and aromatic nucleophilic substitution, alkylation, oxidation, as well as in addition and elimination reactions. These reactions are usually performed in homogeneous solutions or in heterogeneous phase transfer catalysis systems [1–5].

Anion reactivity depends very strongly on interactions with surrounding molecules. Cation–anion association and solvent–anion interactions are important factors determining anion reactivity [6]. The influence of various solvents on anion reactivity has been studied [7]. Anionic species are also used for initiation of various polymerization processes.

A great variety of initiators have been used in anionic polymerization including organolithium and organosodium compounds [8] and various organometallic complexes [9]. A great deal of research on anionic polymerization has been done by Quirk and his colleagues [10–17], the recent progress being summarized in his excellent book [18].

In this paper we report on the novel type of anionic polymerization induced by a two-electron transfer. Single electron transfer mechanism in anionic polymerization was published first by Scott [19] and later by Szwarc and his coworkers [20,21]. They demonstrated that sodium naphthalenide was capable of initiating polymerization of styrene, butadiene and isoprene. Radical anions of a monomer were formed as first intermediates in such polymerization.

It has been demonstrated, that alkali metals, such as potassium and sodium, can be dissolved to form blue metal solutions in aprotic etheral solvents, e.g. tetrahydrofuran after addition of a crown ether [22,23]. In contrast to alkali metals dissolved in ammonia, blue solutions of alkali metals in ethers contain not only solvated electrons but also crowned metal cations and anions [24–26].

Such solutions have been used in organic synthesis, as strong reducing agents [27–30] and as initiators of polymerization [31–34]. To achieve reproducibility of the results in these reactions, well-defined metal solutions should be used. Recently, the kinetics of metal dissolution has been examined and the process of a metal dissolution has been rationalized [24–26]. If the contact time between potassium metal and complexant is about 15 min and the solution is separated from the solid metal, the concentration of solvated electrons is very small, of the order of 10^{-4} M, while the concentration of metal anions is equal to that of metal cations and to the concentration of added crown ether (0.1–0.5 M). This means that the concentration of solvated electrons is negligible in this case, the main active species in such solutions being alkali metal ion pairs, e.g. K^+L,K^-,

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according to the equation

$$2M(s) + L \rightarrow M^{+}L + M^{-}$$

where M is the alkali metal, e.g. potassium or sodium, and L is the complexant, e.g. 18-crown-6. Such alkali metal ion pairs: $M^{+}L,M^{-}$ are able to transfer two electrons towards a suitable substrate to form a carbanion:

$$M^{-} \xrightarrow[\text{transfer of 2 electrons}]{\text{substrate (electrophile)}} M^{+} + \text{carbanion} \qquad (1)$$

It is a general reaction, proceeding with electrophiles which are able to accept two electrons and become carbanions.

If an electrophile is added in excess to reaction medium, a carbanion formed at the first step (Eq. (1)) is able to react with the added substrate and initiate the polymerization producing 'living' polymer. This concept of novel carbanionic polymerization induced by alkali metal ion pairs, e.g.

K^{+}/18-crown-6,K^{-}
K^{+}/15-crown-5,K^{-}

is a general one and can be used in polymerization of many monomers. In the previous papers we demonstrated its utility in polymerization of some vinyl monomers as styrene [35,36], methyl methacrylate [37,38], alkyl halides [39], silyl halides [40], as well as in the ring opening polymerization of lactones [41–43], and oxiranes [44]. In all these processes living polymers, as well as copolymers were produced, containing no metal from the initiators have been obtained.

In this paper we present the results of our studies on polymerization of isoprene, initiated by well-defined supramolecular complex of potassium with 18-crown-6 in tetrahydrofuran. The ability of alkali metal complexes solubilized in an etheral solvent to act as efficient anionic initiators and the 'living' character of the polymers formed are demonstrated.

2. Experimental section

2.1. Materials

Isoprene (Aldrich) was dried over calcium hydride and then distilled under argon before use. 18-crown-6 was purified as described previously [24,25]. THF was purified as described in Ref. [45] and then distilled over a sodium–potassium alloy in atmosphere of dry argon.

2.2. Preparation of the initiator

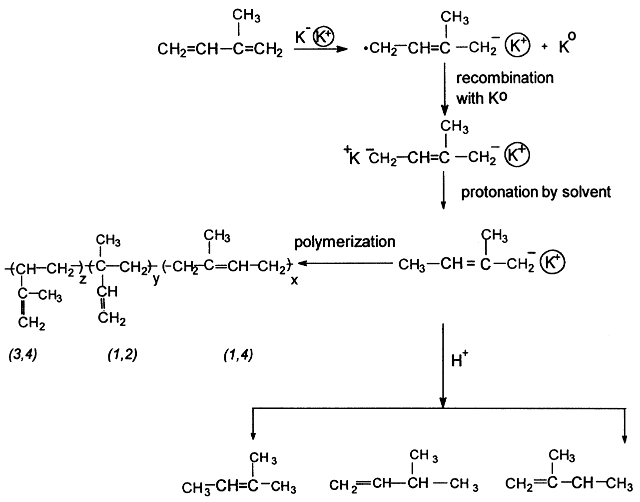
The 0.03 mol/l THF solution of supramolecular complex of potassium was obtained by the contact of the potassium mirror with a solution of 18-crown-6 in THF (0.03 mol/l) for 15 min at temperature 20 °C under inert gas atmosphere. The dissolved potassium complex consisted of potassium ion pairs: K^{+}crown,K^{-}. After 15 min the resulting blue mixture was filtered through a coarse frit to the thermostated glass reactor.

2.3. Polymerization

The polymerization was conducted in THF at 10 °C. A calculated amount of the solution of an initiator was introduced into the thermostated glass reaction chamber and next the solution of isoprene in THF was slowly added. The concentrations of monomers and initiators are provided in Table 2. After completion of polymerization (5 min) the polymer was precipitated by the addition of methanol. The precipitate was washed with methanol several times, dried under vacuum and was kept in darkness at −10 °C. The results of polymerization are presented in Table 2.

2.4. Measurements

The structure of polymers was analyzed by ^{1}H NMR spectroscopy, using a Varian VXR-300 Multinuclear spectrometer. Number average molecular weights were determined by VPO technique in $CHCl_3$ using Knauer vapor pressure osmometer and by GPC. The molecular weight distribution of obtained polymers was determined by GPC according to polyisoprene standards with low polydispersity (Polymer Source, Inc.). GPC experiments were conducted in THF at 35 °C, using the Spectra-Physics 8800 gel permeation chromatograph. Electrospray mass spectrometric (ESI-MS) experiments were carried out using Finnigan LCQ ion trap spectrometer (Finnigan, San Jose, CA, USA). The oligomer sample was dissolved in methanol/chloroform system containing $AgNO_3$, and such solutions were introduced to the ESI source by continuous infusion by means of the syringe pump at a rate of 3 μl/min. The ESI source was operated at 4.25 kV, with the capillary heater at 200 °C, and sheath gas pressure 40 psi. The glass transition temperature (T_g) of polymer samples was



Scheme 1.

Table 1
GC–MS data of protonation and methylation of the model reaction products of isoprene with K^-/K^+,18C6 complex

No.	Products of reaction (after protonation, methylation)	Compound	Characteristic data
1	Protonated product from isoprene reaction	3-Methyl-1-butene 2-Methyl-1-butene 2-Methyl-2-butene	MS *m*/*e*: 70, 55, 43, 40
2	Methylated product from isoprene reaction	2-Methyl-2-pentene 3-Methyl-2-pentene (r) 3,3-Dimethyl-1-butene 2,3-Dimethyl-1-butene	MS *m*/*e*: 84, 69, 57, 54

determined by differential scanning calorimetry (DSC Du Pont 9000 instrument), calibrated with indium and gallium. Samples were heated at 40 °C, cooled to −70 °C, and scanned at the rate of heating 20 °C/min.

3. Results and discussion

Mechanism of the reaction of isoprene with supramolecular complex of potassium was studied. It turned out that in the reaction of isoprene with alkali metal complex two electrons are transferred from the initiator to the isoprene monomer to form dianion, which undergoes instant protonation by the solvent and yields a respective carbanion which is capable of inducing polymerization reaction (Scheme 1). For the sake of simplicity, only one resonance form of a radical anion and dianion are depicted on this scheme.

The main products after protonation in the model reaction of isoprene with the complex of potassium, molar ratio 1:1, are 3-methyl-2-butene, 3-methyl-1-butene and 2-methyl-1-butene (Table 1, Scheme 1). Dianionic species from possible coupling of two radical ions were not found. This suggests a two-electron transfer mechanism.

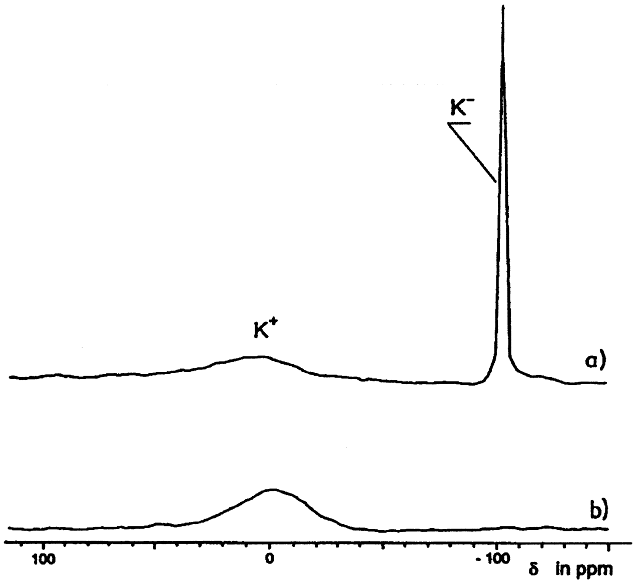


Fig. 1. The ^{39}K NMR spectrum of the potassium complex with 18C6 (a) before the reaction with isoprene and (b) after the reaction.

Another evidence for the transfer of two electrons from the initiator towards monomer at the initiation step was provided by ^{39}K NMR. It was found that the signal of the potassium anion in the ^{39}K NMR spectrum of the metal complex disappeared after the reaction with isoprene, the resonance signal of cation becoming more intense (Fig. 1).

It means that in this reaction the potassium anion, after transferring its two electrons to the isoprene molecule is converted into potassium cation. The occurrence of two-electron transfer steps was suggested previously by Ziegler [46] and by Robertson and Marion [47] in the reaction of metallic sodium with butadiene. They showed the presence of a monomeric disodium adduct in this type of diene polymerization, however, the unambiguous experimental evidence was not provided.

The analysis of the polyisoprene ^1H NMR spectra (Fig. 2) indicates, that the polymerization leads to polymers containing ca. 37% (1,4); 34% (3,4) and 29% (1,2) chain structures.

The results of isoprene polymerization initiated with K^-/K^+,18C6 complexes in THF at 10 °C are shown in Table 2.

It was found that at room temperature the anionic polymerization of isoprene initiated by supramolecular

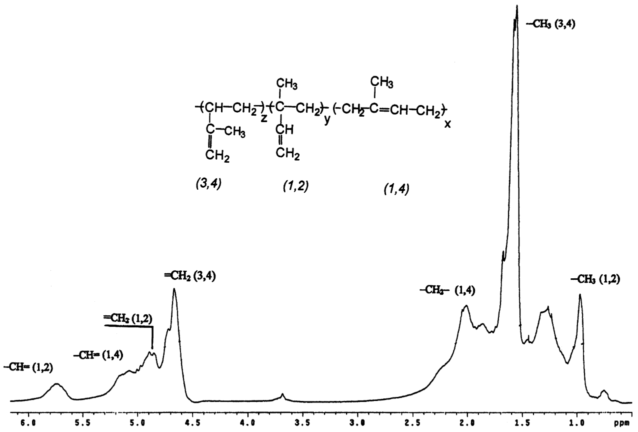


Fig. 2. The ^1H NMR (300 MHz) spectrum of polyisoprene polymer obtained in the presence of supramolecular complex of potassium in THF, at 10 °C.

Table 2
Homopolymerization of isoprene initiated by K^-/K^+,18C6 complex at 10 °C

Alkali metal[a]	I_0 (mol/l)	m_0 (mol/l)	M_n (× 10^{-3}) (expt.)[b]	M_n (× 10^{-3}) (calc.)[c]	M_w/M_n	T_g (°C)	Isomers (%)		
							1,2	3,4	1,4
K	0.00319	0.2528	4.98	5.38	1.6		29.4	33.8	36.8
K	0.00689	1.2146	11.49	12.00	1.4		23.4	28.9	47.7
K	0.00416	0.9890	15.83	16.20	1.7	− 1.6			
K	0.00625	2.9148	31.63	31.77	2.1				
K	0.00551	3.091	33.47	38.19	1.7	− 5.3	27.5	29.1	43.4
K	0.00081	1.5456	125.52	130.0	1.8	9.7	29.4	35.3	35.3
K	0.00096	4.7342	315.80	335.97	2.1				

[a] Alkali metal complex obtained from K mirror by dissolution in THF containing 18-crown-6. Metal complex forms in solution ion pairs, e.g. K^+crown,K^-. Preparation of initiators is described in Section 2.

[b] Estimated by GPC using polyisoprene standards with low polydispersity and similar microstructure (Polymer Source, Inc.).

[c] Calculated from $(m_0/I_0) \times M$ (where m_0, I_0 are the initial concentrations of monomer and initiator, respectively, and M is the molecular weight of the monomer).

complex of potassium in THF proceeds fast and polymers obtained exhibit high molecular weights up to 315 000. In order to demonstrate the living character of this process, polymerization of isoprene in THF at 10 °C, has been carried out at various monomer/initiator molar ratios. A linear dependence of experimental molecular weights and calculated ones is observed for a broad molecular weight range. Thus, the molecular weight of

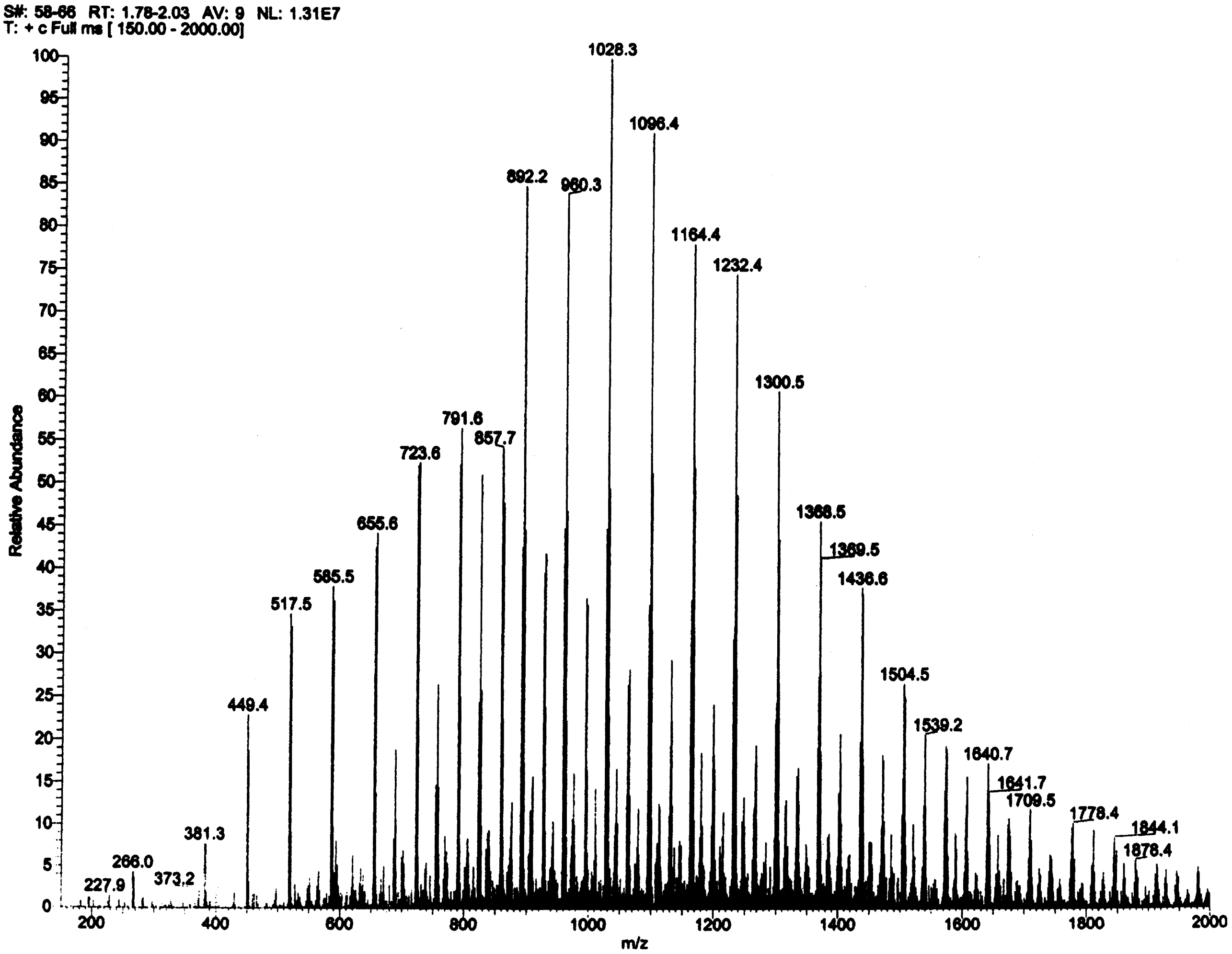


Fig. 3. The ESI-MS spectrum (positive-ion mode) of polyisoprene polymer obtained in polymerization initiated by supramolecular complex of potassium in THF, at 10 °C ($M_n = 899$).

polymers could be controlled by changing the ratio of initial concentrations of the monomer and the initiator as shown in Table 2. The number average molecular weight of the polymer was in good agreement with the expected value. In all cases high conversions up to 100% were observed. Polydispersity of synthesized polymers was (1.4–2.1). The rather large polydispersity values are probably due to the increased temperature and the high exothermic effect in very viscose medium of the reaction.

In the ESI-MS spectra (Fig. 3), the peaks are characterized by increment of 68.12 Da from one peak to the next, which is equal to the mass of the repeating isoprene unit.

4. Conclusions

The anionic polymerization of isoprene in the presence of novel initiator—supramolecular complex of potassium with 18-crown-6 in THF (K^-/K^+,18C6), has been studied. The described supramolecular catalyst is extremely convenient because it works perfectly at room temperature yielding polymers with molecular weights up to 315 000 and with polydispersity (1.4–2.1). The ^{1}H NMR and ESI-MS have been used to determine the structure of the resulting polymer. The microstructure of the above synthesized polyisoprene showed 37% of 1,4 units; 34% of 3,4 units and 29% of 1,2 units.

This novel catalyst system produces carbanions as intermediates and polymers with desired structure and molecular weight containing no traces of catalysts.

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